

## PATENT ABSTRACTS OF JAPAN

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## (54) METHOD FOR PURIFYING POLYSTYRENE BROMINATION SOLUTION

## (57)Abstract:

PURPOSE: To completely and easily remove hydrogen bromide and a Friedel- Crafts catalyst from the bromination soln. to thereby obtain a brominated poly styrene excellent in heat resistance by putting the soln. into a specified amt. of water in the process for producing the brominated polystyrene by reacting polystyrene with bromine in an org. solvent in the presence of the catalyst.

CONSTITUTION: Polystyrene having a wt. average mol. wt. of 10,000-5000,000 is brominated and purified by dissolving the resin in an org. solvent, pref. a satd. aliph. halogenated hydrocarbon (e. g. methylene chloride), adding a Friedel-Crafts catalyst (e. g. aluminum chloride) to the resin soln. in an amt. of 1-10mol% based on the benzene ring of the resin, adding a brominating agent (e. g. bromine) in an amt. of 1-3.3mol based on 1mol of the benzene ring of the resin dropwise to the soln. to brominate the resin, putting the reaction soln. into 0.3-10 times as much water after completion of the bromination, and extracting the water layer with the solvent.

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CLAIMS

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[Claim(s)]

[Claim 1] The purification approach of the polystyrene bromination reaction solution characterized by facing making a bromine react to the bottom polystyrene of existence of an Friedel Crafts reaction catalyst in an organic solvent, and manufacturing bromination polystyrene, and throwing a bromination reaction solution into underwater [ twice / 0.3 - 10 weight / as many as this reaction solution ].

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the purification approach of a polystyrene bromination reaction solution. Furthermore, the hydrogen bromide generated by the reaction and an Friedel Crafts reaction catalyst are removed from a polystyrene bromination reaction solution completely easily in detail, and it is related with the purification approach of a polystyrene bromination reaction solution that bromination polystyrene excellent in thermal resistance useful as a flame retarder is obtained.

[0002]

[Description of the Prior Art] Conventionally, the method of making a bromine react to the bottom polystyrene of existence of a Friedel-Crafts catalyst in an organic solvent is learned as a manufacturing method of bromination polystyrene. A hydrogen bromide is generated in this reaction. It has removed by adding the alkali water solution of the specified quantity in the reaction solution generated after the reaction, and conventionally, neutralizing in it as indicated by JP,2-215807,A. However, since the metal hydroxide generated by neutralization of an Friedel Crafts reaction catalyst is insoluble to water or an organic solvent according to this approach, it comes to mix into a product. If this metal hydroxide mixes into a product, in order to have a great bad influence on the thermal resistance of a product, the process which removes these is needed. And the filtration and liquid separation of a reaction solution of these removal are inadequate.

[0003] Removing a hydrogen bromide and a Friedel-Crafts catalyst is known by repeating several back times rinsing to which water was added to the reaction solution and deactivation of the catalyst was carried out as an approach of solving the above-mentioned technical problem. However, by this approach, in case water is added, a rapid temperature rise happens with generation of heat by deactivation of a catalyst, and the heat of dissolution to the water of the hydrogen bromide in a reaction solution, and it has a bad influence on the hue of a product. Moreover, since separation with the aqueous phase worsens, the phenomenon in which removal of a by-product becomes difficult arises. So, the product obtained is unsatisfying in quality. In addition, by this approach, in order to add water into a reaction container, it is necessary to dry a reaction container for every batch, and there is also a problem of taking a long time to obtain a product.

[0004]

[Problem(s) to be Solved by the Invention] This invention removes completely easily the hydrogen bromide generated by the reaction, and an Friedel Crafts reaction catalyst from the polystyrene bromination reaction solution which a bromine is made to react to the bottom polystyrene of existence of an Friedel Crafts reaction catalyst, and is obtained in an organic solvent, and aims at offering the purification approach of a polystyrene bromination reaction solution that bromination polystyrene excellent in thermal resistance useful as a flame retarder is obtained.

[0005] It becomes possible to carry out deactivation of the catalyst for a short time by pouring in the reaction solution generated in the container which prepared the water of the amount of specification as a result of this invention person's attaining the above-mentioned purpose and inquiring wholeheartedly. The rapid temperature rise of a reaction solution could be avoided, separation with a reaction solution and the aqueous phase became very good, the reaction container could also be used continuously, and a header and this invention were reached [ that all the above-mentioned technical problems -- the bromination polystyrene which was moreover excellent in thermal resistance is obtained -- can be solved, and ].

[0006]

[Means for Solving the Problem] This invention is the purification approach of the polystyrene bromination reaction solution characterized by throwing into underwater [ twice / 0.3 - 10 weight / as many as this reaction solution ] the

polystyrene bromination reaction solution which a bromine is made to react to the bottom polystyrene of existence of an Friedel Crafts reaction catalyst, and is obtained in an organic solvent.

[0007] As an organic solvent used for the target polystyrene bromination reaction, saturation aliphatic series halogenated hydrocarbon, such as a methylene chloride, a dichloroethane, trichloroethane, tetrachloroethane, dichloro dibromoethane, dibromoethane, tetrabromo ethane, and a carbon tetrachloride, is raised with the purification approach of this invention, for example. Not only an anhydrous solvent but when it collects so that it may usually be carried out industrially, and it contains moisture, these may carry out dehydration processing and may be the solvents of an anhydrous condition substantially. Especially in these solvents, a methylene chloride is desirable.

[0008] As a Friedel-Crafts catalyst, an aluminum chloride, the aluminium bromide, ferric chloride, iron bromide, etc. are raised, for example, and these are independent or may be used with two or more sorts of mixture. Especially an aluminum chloride is desirable also in these catalysts. since the amount of the catalyst used has the inclination for reaction time to become long if too few, and for coloring of the bromination polystyrene which will be obtained if it is made [ many / too much ] to become large -- 1-10 mol % of usual [ per one mol of benzene rings of polystyrene ] -- it is 2-6-mol % preferably.

[0009] As polystyrene, about 10,000 to 500,000 thing is usually used with weight average molecular weight, and the thing of 20,000-250,000 is desirable. Although thermal resistance becomes good in weight average molecular weight having used 10,000 or less thing so that the thermal resistance of the bromination polystyrene obtained comes to fall and weight average molecular weight becomes high, it is to about 500,000 that it can be used practical.

[0010] As for the bromine used as a brominating agent, it is desirable to use 1-3.3 mols to one mol of benzene rings of raw material polystyrene. If the bromine content of bromination polystyrene becomes inadequate and it is made [ more ] than 3.3 mols when fewer than one mol, residual bromines increase in number at the time of reaction termination, and it is not economical.

[0011] In order to make a bromine react to polystyrene, polystyrene is first dissolved in said aliphatic series halogenated hydrocarbon solvent completely, and a bromine is added after adding the Friedel-Crafts catalyst of the specified quantity subsequently. A bromination reaction is performed by holding preferably 0-30 degrees C of temperature at 5-20 degrees C, and dropping a bromine. There is an inclination for coloring of the bromination polystyrene from which it will be obtained if a rate of reaction becomes slow at less than 0 degree C and reaction temperature is higher than 30 degrees C to become large. It holds at further 5-15 degrees C after dropping termination, stirring is continued for 1 to 2 hours, and a reaction is completed.

[0012] If it is in this invention, after feeding into the water of the specified quantity the reaction solution obtained after reaction termination, carrying out deactivation of the catalyst and separating the aqueous phase, an organic solvent phase is washed further and an impurity is removed. The amount of water which throws in a reaction solution is 0.3 - 10 weight twice to reaction solution weight, and its 0.7 - 3 weight twice are desirable. It is not economical for a reaction solution to be heated locally, and to spoil the quality of bromination polystyrene, or for separation with the aqueous phase to come to get worse, and to make [ more ] it than 10 weight twice with the heat of dissolution of the hydrogen bromide whose amount of water is the catalyst and by-product which are contained in the reaction solution less than [ of the amount of reaction solutions / 0.3 weight twice ]. As for water temperature, it is desirable that it is 0 degree C - 30 degrees C.

[0013] In addition, when the bromine remains in the reaction solution, it is desirable to wash using the water which added the reducing agent like a sodium thiosulfate or a sodium sulfite. It is good also by the approach which may fill the saturated aliphatic hydrocarbon of lower alcohol, such as the approach of arbitration, for example, a methanol etc., or carbon numbers 5-8 with an organic solvent phase for isolating the bromination polystyrene contained in the organic solvent phase after washing, may be deposited, and distills off a solvent under the vacuum like spray drying.

[0014] Since the bromination polystyrene obtained by the approach of this invention has 1-3 bromine atoms per benzene ring and is excellent in thermal resistance, it is very useful as flame retardants of plastics, such as a polycarbonate, polyester, polypropylene, styrene resin, and a polyamide.

[0015]

[Example] An example is raised to below and it explains to it further. In addition, the section in an example and % are weight section and weight %. Carry out the dryblend of the bromination polystyrene obtained in each example and the example of a comparison in the C-3030]100 section, extrude it, and the ten sections and the antimony-trioxide [ ATOX-S by NIHON SEIKO CO., LTD.] 5 section are pelletized. thermal resistance -- strengthening polyethylene-terephthalate-resin [-- Teijin, Ltd. make [ ] -- The test piece with a thickness of 3.2mm was fabricated for this pellet at 290 degrees C of cylinder temperatures with the injection molding machine, shaping was suspended during shaping, postforming made to pile up for 15 minutes at 290 degrees C was resumed, and b value of the test piece before and

behind stagnation was measured in color meter. It is shown that thermal resistance is so bad that b value is so large that the difference of b value before and behind stagnation is large.

[0016]

[Example 1] The methylene chloride 260 section and the polystyrene [Dainippon Ink ERASUCHIREN 200 and weight-average-molecular-weight 55,000] 17 section were taught to the reaction vessel, it held at 10 degrees C, the bottom aluminum chloride of stirring 0.7 section was supplied, subsequently the bromine 55 section was dropped over 2 hours, it stirred after dropping termination for further 1 hour, and the reaction was completed. It poured into it under stirring, having reaction covered [ which was obtained ] it over the container which prepared the water of the 400 sections for 15 minutes, and deactivation of the catalyst was carried out. The aqueous phase was removed and the water of the 400 sections washed the organic solvent phase twice. The removed aqueous phase was transparent. The centrifugal separator separated the solid-state which trickled having applied the organic solvent phase to the methanol of the 600 sections under stirring for 3 hours, and deposited, it dried, and the bromination polystyrene (63% of bromine contents) 40.2 white section was obtained. The heat-resistant evaluation result was shown in Table 1.

[0017]

[Example 2] The methylene chloride 260 section and the polystyrene [Dainippon Ink ERASUCHIREN 200 and weight-average-molecular-weight 55,000] 17 section were taught to the reaction vessel, it held at 10 degrees C, the bottom aluminum chloride of stirring 0.7 section was supplied, subsequently the bromine 66 section was dropped over 2 hours, it stirred after dropping termination for further 1 hour, and the reaction was completed. It poured into it under stirring, having reaction covered [ which was obtained ] it over the container which prepared the water of the 400 sections for 15 minutes, and deactivation of the catalyst was carried out. The aqueous phase was removed and the water of the 400 sections washed the organic solvent phase twice. The removed aqueous phase was transparent. The centrifugal separator separated the solid-state which trickled having applied the organic solvent phase to the methanol of the 600 sections under stirring for 3 hours, and deposited, it dried, and the bromination polystyrene (66% of bromine contents) 48.7 white section was obtained. The heat-resistant evaluation result was shown in Table 1.

[0018]

[Example 3] The bromination polystyrene (63% of bromine contents) 38.9 white section was obtained like the example 1 except making into the 1000 sections amount of water taught to a container.

[0019]

[The example 1 of a comparison] The methylene chloride 260 section and the polystyrene [Dainippon Ink ERASUCHIREN 200 and weight-average-molecular-weight 55,000] 17 section were taught to the reaction vessel, it held at 10 degrees C, the bottom aluminum chloride of stirring 0.7 section was supplied, subsequently the bromine 55 section was dropped over 2 hours, it stirred after dropping termination for further 1 hour, and the reaction was completed. In addition, deactivation of the catalyst was carried out to it, having poured the water of the 50 sections on the obtained reaction solution for 90 minutes. The aqueous phase was removed and sequential washing of the organic solvent phase was carried out once 3 times in the water 200 section by the sodium-hydroxide water-solution 200 section 10%. The removed aqueous phase was white translucence. It was dropped having applied the organic solvent phase to the methanol of the 600 sections under stirring for 3 hours, the centrifugal separator separated the depositing solid-state, it dried, and the bromination polystyrene (62% of bromine contents) 39.1 white section was obtained. The heat-resistant evaluation result was shown in Table 1.

[0020]

[The example 2 of a comparison] The methylene chloride 260 section and the polystyrene [Dainippon Ink ERASUCHIREN 200 and weight-average-molecular-weight 55,000] 17 section were taught to the reaction vessel, it held at 10 degrees C, the bottom aluminum chloride of stirring 0.7 section was supplied, subsequently the bromine 55 section was dropped over 2 hours, it stirred after dropping termination for further 1 hour, and the reaction was completed. It was dropped at it, having applied [ water 50 ] it to the obtained reaction solution for 15 minutes, and deactivation of the catalyst was carried out. The aqueous phase was removed and the water of the 400 sections washed the organic solvent phase 3 times. The removed aqueous phase is white translucence and existence of an interlayer was accepted. It applied for 3 hours to the bottom of stirring to the methanol of the 600 sections of an organic solvent phase, and was dropped, the centrifugal separator separated the depositing solid-state, it dried, and the bromination polystyrene (62% of bromine contents) 39.6 white section was obtained. The heat-resistant evaluation result was shown in Table 1.

[0021]

[The example 3 of a comparison] The methylene chloride 260 section and the polystyrene [Dainippon Ink ERASUCHIREN 200 and weight-average-molecular-weight 55,000] 17 section were taught to the reaction vessel, it

held at 10 degrees C, and the bottom aluminum chloride of stirring 0.7 section was supplied. Subsequently, the bromine 66 section was dropped over 2 hours, it stirred after dropping termination for further 1 hour, and the reaction was completed. It poured into it under stirring, having reaction covered [ which was obtained ] it over the container which prepared the water of the 80 sections for 15 minutes, and deactivation of the catalyst was carried out. The aqueous phase was removed and the water of the 200 sections washed the organic solvent phase 5 times. The removed aqueous phase was transparent. The centrifugal separator separated the solid-state which trickled having applied the organic solvent phase to the methanol of the 600 sections under stirring for 3 hours, and deposited, it dried, and the bromination polystyrene (66% of bromine contents) 47.8 yellow section was obtained. The heat-resistant evaluation result was shown in Table 1.

[0022]

[Table 1]

	耐 熱 性	
	滞 留 前 (b 値)	滞 留 後 (b 値)
実施例 1	8. 5	10. 2
実施例 2	9. 2	12. 9
実施例 3	8. 8	11. 0
比較例 1	15. 7	22. 3
比較例 2	11. 7	18. 3
比較例 3	12. 3	19. 5

[0023]

[Effect of the Invention] The effectiveness that become possible to carry out deactivation of the reaction catalyst for a short time according to the approach of this invention, and can avoid the rapid temperature rise of a reaction solution, and separation with a reaction solution and the aqueous phase becomes very good, can use a reaction container continuously, bromination polystyrene useful as a flame retarder which was moreover excellent in thermal resistance is obtained, and this invention does so is exceptional.

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behind stagnation was measured in color meter. It is shown that thermal resistance is so bad that b value is so large that the difference of b value before and behind stagnation is large.

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